

## Solute Type and Viscosity of Dilute Solutions of High Polymers

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FRITH<sup>2,3</sup> has recently considered the theoretical significance of the slope of  $\eta_{sp}/c - c$  curves for solutions of high polymers. By statistical and quasithermodynamical analysis, she has shown that the slope is related to the energy of polymer-solvent interaction, the slope being greater for a good solvent or solvent mixture than for a poor one.<sup>2,4</sup> Frith has also shown that at low concentrations her equation for the variation of  $\eta_{sp}/c$  with  $c$  is similar to Huggins'.<sup>5</sup>

In Huggins' equation the slope,  $k'[\eta]^2$ , is proportional to the square of the intrinsic viscosity, and the constant,  $k'$ , is characteristic, and independent<sup>4,5</sup> of the intrinsic viscosity for a given polymer-solvent system. This invariance of  $k'$  makes it a more useful quantity for discussion than the slope. For this reason we have combined Frith's and Huggins' equations to obtain the following relation among the constants:

$$k' = B'/[\eta]^2 - Bw/[\eta]^2 kT = A - B''w/T, \quad (1)$$

where  $A$  and  $B''$  are independent of  $[\eta]$ .

The second term accounts for the variation of  $\eta_{sp}/c$  with concentration due to the energy of interaction,  $w$ , between the polymer chain segment and solvent molecules, whereas the first term accounts for variations with concentration due to other causes, such as differing internal structure.  $w$  is negative<sup>2</sup> when a tendency exists for solvation of the polymer chain segment. Thus, if a solvent is made inferior by addition of a non-solvent, which leads to a less negative  $w$ ,  $k'$  decreases; if a better solvent is used,  $w$  has a more negative value and  $k'$  increases. Likewise, if the energy of interaction is constant and only the internal structure is changed,  $k'$  varies with  $A$ .

Variations of  $k'$  can be divided into two cases: (1) the interaction energy,  $w$ , remains constant and  $A$  varies; (2)  $A$  remains constant and  $w$  varies by changing (a) the solvent or (b) the solute type. Case 2(b) is often trivial but becomes important when one studies the change in polymer-solvent interaction as the nature of the surface of the molecule is changed.

Numerous examples of Case 2(a) may be found in the literature.<sup>2,4,5</sup> A possible example of Case 1 was the ob-

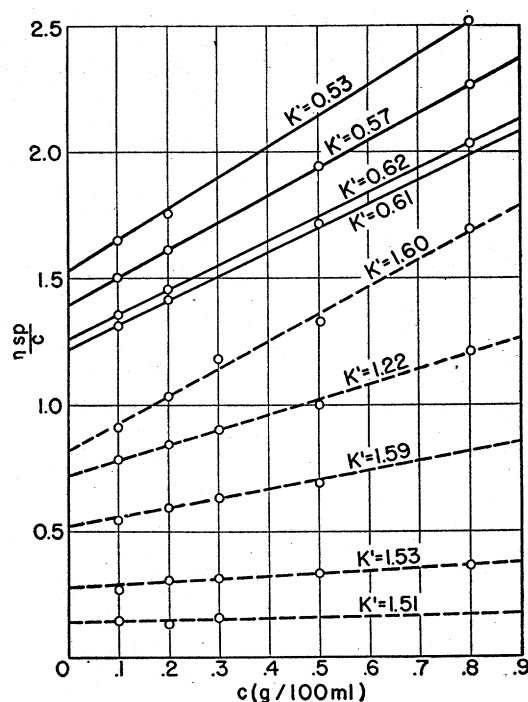


FIG. 1.  $\eta_{sp}/c - c$  curves for potato amylose and amylopectin fractions in 2 percent KOH. Solid lines amylose. Dashed lines amylopectin. Amylose and amylopectin were separated from whole starch with nitrobenzene. (See reference 8.) Amylose components (and amylopectin components) were fractionally precipitated by isopropyl alcohol from 0.5 percent KOH.

servation of Bartovics and Mark<sup>6</sup> on polystyrene that  $k'$  changes with the temperature of polymerization. This variation in  $k'$  was attributed to a change in the internal structure of the polystyrene as a result of a change in the mechanism of polymerization with the temperature.

We have obtained viscosity data which provide good examples of Cases 1 and 2(b). Figure 1 represents  $\eta_{sp}/c - c$  curves for fractionated potato amylose and amylopectin (Case 1). It is evident that  $k'$  (computed from Huggins'

equation) for amylose (linear chain) and amylopectin (branched chain) fractions, respectively, is independent of the intrinsic viscosity. However,  $k' = 0.58 \pm 0.02$  for amylose<sup>7</sup> is considerably less than  $k' = 1.49 \pm 0.10$  for amylopectin. These two substances have a well-recognized difference in molecular structure. Since both amylose and amylopectin are composed of glucose residues,  $w$  for amylose and amylopectin must be nearly identical, and the difference in  $k'$  must be due to a difference in  $A$  for the two molecules. These results suggest that this method may provide a means of detecting branching in high polymers.

Case 2(b) is illustrated by pectin nitrate solutions in acetone for which Table I lists average values of  $k'$  for five fractions. Two samples were used, their degree of methyl esterification before nitration being 0.75 and 0.24. The  $k'$ 's for the pectin nitrate fractions obtained from each sample are independent of the intrinsic viscosity, but  $k'$  for "high ester" pectin nitrate is greater than that for "low ester" pectin nitrate. In this example, the solute molecule is principally altered through replacement of methyl ester groups by carboxyls, thus changing polymer-solvent interaction, with consequent variation of  $k'$ . Because methyl ester groups are more compatible with acetone than carboxyl groups,  $k'$  for pectin nitrate made from the untreated pectin is greater than  $k'$  for the acid deesterified pectin nitrate.

TABLE I.— $k'$  values calculated from  $\eta_{sp}/c - c$  curves for pectin nitrate-acetone solutions.

Treatment of pectin sample before nitration	Degree <sup>b</sup> of methyl esterification	$k'$	$N$
Untreated	0.75 <sup>c</sup>	$0.87 \pm .02^d$	9.4%
Acid deesterified <sup>a</sup>	0.24 <sup>c</sup>	$0.19 \pm .02^d$	9.4

<sup>a</sup> For method, see C. H. Hills, J. W. White, Jr., and G. L. Baker, *Proc. Inst. Food Tech.* page 47 (1942).

<sup>b</sup>  $\lambda = [\text{COOCH}_3]/([\text{COOH}] + [\text{COOCH}_3])$ ; C. H. Hills and R. Speiser, *Science*, in press.

<sup>c</sup> Degree of methyl esterification before nitration. Nitration results in approximately 30 percent methyl deesterification.

<sup>d</sup> Average for five fractions of different intrinsic viscosity.

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<sup>2</sup> E. M. Frith, *Trans. Faraday Soc.* **41**, 17, 90 (1945).

<sup>3</sup> E. M. Frith and R. F. Tuckett, *Nature* **155**, 164 (1945).

<sup>4</sup> T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.* **64**, 1557 (1942).

<sup>5</sup> M. L. Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942).

<sup>6</sup> A. Bartovics and H. Mark, *J. Am. Chem. Soc.* **65**, 1901 (1943).

<sup>7</sup> Data of J. F. Foster and R. M. Hixon, *J. Am. Chem. Soc.* **65**, 618 (1943), yield  $k' = 0.62, 0.67, 0.57$ , and  $0.65$  for whole potato amylose, whole tapioca amylose, whole lily bulb amylose, and whole corn amylose, respectively. This agreement with our data for amylose is noteworthy, since Foster and Hixon's solvent was anhydrous ethylene diamine, whereas we used 2 percent KOH.

<sup>8</sup> R. L. Whistler and G. E. Hilbert, "Theory of the Fractionation of Starch. Separation of Amylose and Amylopectin by Means of Some Nitroparaffins." Unpublished manuscript at the Northern Regional Research Laboratory.